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Claims

1. A polymerization process, comprising:

polymerizing one or more radically (co)polymerizable monomers in the presence of a system comprising;

an initiator comprising one or more radically transferable atom(s) or group(s),

a catalyst system comprising:

a transition metal;

one or more counterions;

a ligand attached to a solid support, wherein the ligand is a N-, O-, P-, or S- containing ligand which can coordinate in a σ-bond to the transition metal or a carbon-containing ligand which can coordinate in a π-bond to the transition metal; and

a soluble ligand, wherein the soluble ligand is a N-, O-, P-, or S-containing ligand which can coordinate in a σ-bond or a carbon-containing ligand which can coordinate in a π-bond to the transition metal to form a soluble transition metal complex.

2. The process of claim 1, wherein the ligand attached to the solid support is

physico- or physicochemically or chemically bound to the surface of the solid support through ionic bonding, physisorption, chemisorption, Van der Waals forces, coordinate or covalent bonding.

3. The process of claim 1, wherein the catalyst system comprises a immobilized transition metal complex, wherein the immobilized transition metal complex is physically, physicochemically or chemically attached to the solid support through ionic bonding, physisorption, chemisorption, Van der Waals forces, coordinate or covalent bonding through though a functional group on the ligand.

4. The process of claim 2, wherein the ligand attached to the solid support forms the immobilized transition metal complex with at least a portion of the transition metal.

5. The process of claim 4, wherein the soluble ligand and at least a portion of the transition metal form a soluble transition metal complex.

6. The process of claim 5, wherein at least a portion of the soluble transition metal complex comprises a higher oxidation state.

7. The process of claim 2, wherein the solid support comprises an ion exchange resin.

8. The process of claim 7, wherein the ion exchange resin is based on polystyrene.

9. The process of claim 2, wherein the solid support is an inorganic material.

10. The process of claim 9, wherein the inorganic solid is a silica, an alumina or a clay.

11. A polymerization process, comprising:

polymerizing one or more radically (co)polymerizable monomers in the presence of a system comprising;

an initiator comprising one or more radically transferable atom(s) or group(s),

an attached transition metal complex comprising

a transition metal;

one or more counterion(s);

a ligand attached to a solid support, wherein the ligand is a N-, O-, P-, or S- containing ligand which can coordinate in a σ-bond or a carbon-containing ligand which can coordinate in a π-bond to the transition metal;

a soluble transition metal complex comprising:

a transition metal;

a soluble ligand wherein the ligand is a N-, O-, P-, or S- containing ligand which can coordinate in a σ-bond or a carbon-containing ligand which can coordinate in a π-bond to the transition metal, wherein the

transition metal comprises the redox conjugate of the attached transition metal complex; wherein at least one of the attached transition metal complex and a soluble transaction metal complex participate in a reversible redox cycle with at least one of the initiator or a compound having a radically transferable atom or group.

12. The process of claim 11, wherein the solid support is an inorganic material.

13. The process of claim 12, wherein the solid support is a silica, an aluminate or a clay.

14. The process of claim 11, wherein the solid support is an organic material.

15. The process of claim 14, wherein the solid support is an ion exchange resin.

16. The process of claim 15, wherein the ion exchange resin is based on polystyrene.

17. The process of claim 11, wherein one or more of the N-, O-, P-, or S- containing ligand(s) which can coordinate in a σ-bond, or a carbon-containing ligand which can coordinate in a π-bond to the transition metal are chemically bonded to the solid support.

18. The process of claim 11, wherein the process is conducted in a batch reactor.

19. The process of claim 11, wherein the process is conducted in a continuous flow system.

20. The process of claim 11, further comprising:

introducing a reducing agent.

21. The process of claim 20, wherein the reducing agent is a source of free radicals.

22. The process of claim 20, reducing agent comprises a transition metal in the zero oxidation state.

23. The process of claim 11, wherein the ligand attached to the solid support comprises one or more substituant(s) that adsorb on the solid support.

24. A controlled polymerization process of atom or group transfer polymerization, comprising:

polymerizing one or more radically (co)polymerizable monomers in the presence of a system initially comprising;

an initiator comprising one or more radically transferable atom(s) or group(s),

a transition metal complex comprising a transition metal and one or more counterion(s) which interacts with a N-, O-, P-, or S- containing ligand which can coordinate in a σ-bond to the transition metal or a carbon-containing ligand which can coordinate in a π-bond to the transition metal, wherein the ligand is additionally physico- or physicochemically or chemically bound to the surface of a

solid support through ionic bonding, physisorption, chemisorption, Van der Waals forces, coordinate or covalent bonding; and

changing at least one (co)polymerization condition to cause at least a portion of the transition metal complex to be unbound from the surface of the solid support.

25. The process of claim 11, wherein at least one of the soluble transition metal complex and the soluble ligand is present at less than 25 mole % of the ligand that is attached to the solid support.

26. The process of claim 11, wherein at least one of the soluble transition metal complex and the soluble ligand is present at less than 3 mole % compared to the ligand that is attached to the solid support.

27. The process of claim 11, wherein at least a portion of the transition metal compound comprises a radically transferable atom or group and is in a higher oxidation state, and further comprising:

forming the initiator by transferring the radically transferable atom or group from the transition metal compound in a higher oxidation state to a free radical.

28. A process for the removal and recycle of a supported transition metal catalyst complex from a polymerization reaction medium comprising the steps:

separating the supported transition metal catalyst from the reaction medium, and

contacting the supported transition metal catalyst with a reducing agent.

29. The process of claim 28, wherein the reducing agent is a transition metal in a zero oxidation state.

30. The process of claim 28, wherein the reaction medium comprises a solvent.

31. The process of claim 15, wherein the ion exchange resin comprises a crosslink density and a bead size, wherein at least one of the crosslink density and the bead size is chosen to enhance access of the polymerization medium to the attached catalyst complex.

32. The process of claim 11, wherein the system comprises at least one of a solution, emulsion or miniemulsion.

33. The process of claim 32, wherein the solution, emulsion or miniemulsion comprises an inorganic liquid.

34. The process of claim 32, wherein the solution, emulsion or miniemulsion comprises water.

35. The process of claim 15, wherein a reaction medium comprises the monomers, initiator, and soluble ligand and the reaction medium is passed over a bed of the ion exchange medium.

36. The process of claim 15, further comprising:

separating the ion exchange medium from the system.

37. The process of claim 28, further comprising:

recycling the supported transition metal catalyst.

38. The process of claim 15, wherein an equilibrium between the soluble transition metal complex and attached transition metal complex is controlled at least one of the polarity of the reaction medium, ionic character of the ion exchange resin, pH of the system, degree of crosslinking of the ion exchange resin, swellability of the ion exchange resin, permeability of the ion exchange resin, acid strength of the supported counterion, gross size of the ion exchange resins, the oxidation state and molar excess of transition metal complexes or ligand present in the system.

39. A polymerization process comprising:

providing an immobilized catalyst comprising:

a transition metal;

one or more counterions;

a ligand attached to a solid support, wherein the ligand is a N-, O-, P-, or S- containing ligand which can coordinate in a σ-bond to the transition metal or a carbon-containing ligand which can coordinate in a π-bond to the transition metal; introducing radically polymerizable monomers to the immobilized catalyst system; and

adding a soluble ligand, wherein the soluble ligand is a N-, O-, P-, or S-containing ligand which can coordinate in a σ-bond or a carbon-containing ligand which can coordinate in a π-bond to the transition metal.

40. A polymerization process comprising:

providing an immobilized catalyst comprising:

a transition metal;

one or more counterions;

a ligand attached to a solid support, wherein the ligand is a N-, O-, P-, or S- containing ligand which can coordinate in a σ-bond to the transition metal or a carbon-containing ligand which can coordinate in a π-bond to the transition metal; introducing radically polymerizable monomers to the immobilized catalyst system;

introducing a soluble catalyst comprising:

a second transition metal;

one or more second counterions;

a soluble ligand, wherein the soluble ligand is a N-, O-, P-, or S-containing ligand which can coordinate in a σ-bond to the second transition metal or a carbon-containing ligand which can coordinate in a π-bond to the second transition metal to the immobilized catalyst system; and

introducing an initiator to the immobilized catalyst system.

41. The process of claim 11, wherein the soluble ligand is different than the ligand attached to the solid support.